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1 October 1961 - 31 December 1961

RESEARCH ON PHASE EQUILIBRIA BETWEEN BORON  
OXIDES AND REFRACTORY OXIDES, INCLUDING  
SILICON AND ALUMINUM OXIDES

W.C. Beard, W.C. Buttermann, D.E. Koopman  
H. E. Wenden, and W.R. Foster

Aeronautical Systems Division  
Contract AF 33(616)-6509



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**QUARTERLY PROGRESS**

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**THE OHIO STATE UNIVERSITY  
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**To:**

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**On:**

**RESEARCH ON PHASE EQUILIBRIA BETWEEN BORON  
OXIDES AND REFRACTORY OXIDES, INCLUDING  
SILICON AND ALUMINUM OXIDES**

**For the period:**

**1 October 1961 - 31 December 1961**

**Submitted by:**

**W. C. Beard, W. C. Buttermann, D. E. Koopman,  
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## I. INTRODUCTION

This report summarizes the work done during the tenth quarterly report period, 1 October 1961 to 31 December 1961. During this period attention was directed to the systems  $\text{TiO}_2\text{-B}_2\text{O}_3$ ,  $\text{ZrO}_2\text{-B}_2\text{O}_3$ ,  $\text{HfO}_2\text{-B}_2\text{O}_3$ , and  $\text{ThO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$ .

A literature survey was made for each of these systems. Preliminary experiments of a reconnaissance nature were also carried out. It is proposed to extend these studies so as to secure a phase diagram for each of the systems. Additional information is expected on the polymorphic relations of the refractory oxides  $\text{TiO}_2$ ,  $\text{ZrO}_2$  and  $\text{HfO}_2$ , and on the conditions for successful growth of single crystals.

## II. THE SYSTEM $\text{TiO}_2\text{-B}_2\text{O}_3$

No study designed specifically to establish phase relations in the system  $\text{TiO}_2\text{-B}_2\text{O}_3$  has yet been made. Ebelman<sup>1</sup> failed to obtain compound formation by prolonged heating of titanic oxide with boric acid. Guertler<sup>2</sup> reported that  $\text{TiO}_2$  is dissolved in molten boric acid anhydride and yields an emulsion on cooling. Mixtures from pure  $\text{B}_2\text{O}_3$  to the mol ratio 1 : 1 form homogeneous melts at high temperature, but on cooling, melts within a certain composition range becomes turbid and segregate immediately into two liquid phases. A two-liquid area is thus to be expected in the  $\text{TiO}_2\text{-B}_2\text{O}_3$  phase diagram, but whether it affects the liquidus, or occurs metastably below the liquidus curve, is not known. Foex<sup>3</sup> established the solubility of  $\text{TiO}_2$  in  $\text{B}_2\text{O}_3$  at 1200° C as 4.4 mols in 100 mols of  $\text{B}_2\text{O}_3$ , or 4.8 weight percent. This observation strongly suggests either that the liquidus curve for  $\text{TiO}_2$  rises sharply (almost vertically) from the melting point of  $\text{B}_2\text{O}_3$  in a monotectic relation, or that an even more nearly vertical liquidus rises from a eutectic located very close to the  $\text{B}_2\text{O}_3$  end-member. Dietzel and Tober<sup>4</sup> were unable to decide whether compound formation is to be expected in the system,

although the difference in field strengths of  $\text{TiO}_2$  (1.25) and  $\text{B}_2\text{O}_3$  (1.45) would appear to fall below the 0.30 limit believed necessary for compound formation. Imaska<sup>5</sup> has investigated the range of glass formation of  $\text{B}_2\text{O}_3$  with numerous other oxides, including  $\text{TiO}_2$ . Considerations developed by Glasser, Warshaw and Roy<sup>6</sup> for prediction of the possibility of liquid immiscibility in silicate systems indicate that immiscibility in the  $\text{TiO}_2$ - $\text{B}_2\text{O}_3$  system is likewise probable, and consistent with the early suggestion of Guertler<sup>2</sup>.

There is wide divergence of opinion as to the true relations between the three polymorphs of  $\text{TiO}_2$ , rutile, anatase and brookite. Most investigators, like Osborn<sup>7</sup>, regard rutile as the form stable at all temperatures, with anatase and brookite as metastable forms which change monotropically to rutile. The anatase to rutile transition has been located as low as  $100^\circ \text{C}$ <sup>8</sup> and as high as  $1200^\circ \text{C}$ <sup>9</sup>. The synthesis of brookite has been claimed as low as  $300^\circ \text{C}$ <sup>10</sup> and as high as  $1300^\circ \text{C}$ <sup>11</sup>, with one author assigning a  $800^\circ$ - $1040^\circ$  range<sup>12</sup>. Three separate forms of anatase and of rutile has been reported<sup>13</sup>. Obviously, additional study is called for in order to obtain clarification of these confused and conflicting relationships.

Failure to convert rutile directly to anatase under any laboratory conditions largely accounts for belief in the monotropic nature of the anatase-to-rutile inversion. A preliminary attempt has been made to effect the rutile-to-anatase transition with the aid of a low-melting flux. Rutile in a large excess of lithium nitrate was heated slightly above the  $\text{LiNO}_3$  melting point ( $268^\circ \text{C}$ ). On the assumption that anatase rather than rutile is the phase stable at low temperatures, it was hoped that the more soluble (because less stable) rutile would dissolve in the  $\text{LiNO}_3$  and that the less soluble (because more stable) anatase would precipitate. No evidence of anatase was observed after 3 days, nor was there any evidence of recrystallization or grain growth of the original rutile. It is not even certain

that rutile dissolved in the flux. The results are therefore considered inconclusive, and further runs are scheduled at 300°, 400°, 500°, 600°, etc. in hope that more elevated temperatures will cause substantial solution of rutile, and that reprecipitation of either rutile or anatase will take place on cooling. Other low-melting fluxes may possess greater solvating ability, and will also be tried.

Another approach to the problem of the anatase - rutile relations was the following. Fine-grained rutile obtained by heat treatment of J. T. Baker C. P. anatase was ground in a mechanical mortar under liquid nitrogen for five minutes. Similar treatment has been found by Bredig to change calcite to aragonite. Previously, aragonite had widely been regarded as having a monotropic relation towards calcite, similar to the relation generally believed to exist between anatase and rutile. Thus far, however, no conversion of rutile to anatase has been effected. It is still hoped that more prolonged grinding in liquid nitrogen may produce the rutile-to-anatase transition, even although the density relations of anatase (3.84) and rutile (4.26) would appear unfavorable. In the course of these tests, some data on the sluggishness of the anatase-to-rutile transition at moderate temperatures were obtained. After 41 hours at 640° C, anatase showed no recognizable alteration. An additional 26½ hours at 700° C likewise failed to produce rutile. After further treatment at 950° C for 116 hours, it was found that all of the anatase had been converted to rutile. Earlier preliminary tests by one of the present authors (HEW) indicated the feasibility of synthesizing brookite hydrothermally at low temperatures, by heating saturated solutions of soluble titanium salts and hydrogen peroxide in a steel bomb. A series of experiments is now in progress, in an endeavor to establish brookite - anatase relations in the  $\text{TiO}_2\text{-H}_2\text{O}$  system, comparable to those reported by Osborn<sup>7</sup> for the anatase-rutile relations. The results of these and other preliminary experiments outlined above are presented in Table 1.



TABLE 1

EXPERIMENTS ON THE POLYMORPHIC INVERSION OF  $\text{TiO}_2$ 

Starting Material	Temp. (° C)	Time	Products
Rutile in $\text{LiNO}_3$	270°	3 dys.	Rutile
Rutile	Liquid $\text{N}_2$	5 min.	Rutile
Anatase	640°	41 hrs.	Anatase
Anatase (preceding run)	700°	26½ hrs.	Anatase
Anatase (preceding run)	950°	116 hrs.	Rutile
Potassium Titanium Oxalate and Hydrogen Peroxide	275 ± 25	3 dys.	Brookite and Anatase
Titanium Sulfate and Hydrogen Peroxide	284°	5 dys.	Anatase and Rutile
Titanium Sulfate and Hydrogen Peroxide	200°	3 dys.	Anatase and Rutile
Potassium Titanium Oxalate and Hydrogen Peroxide	274°	3 dys.	Rutile and K-Titanite (?)

Some preliminary studies have been carried out in the system  $\text{TiO}_2 - \text{B}_2\text{O}_3$ . These had a fourfold purpose; to discover whether any intermediate compound is formed, a question left open by Dietzel and Tober; to check the possible existence of a two-liquid area, a feature suggested by the "emulsion" noted by Guertler; to ascertain whether the  $\text{TiO}_2$ -liquidus is close to  $\text{B}_2\text{O}_3$  composition-vertical, as suggested by the solubility data of Foex; and to locate approximately the anatase - rutile transition temperature in the presence of  $\text{B}_2\text{O}_3$ .

Seven mixtures were prepared (Table 2) using Baker's C. P. anatase and Fisher's A-76 fused purified boric acid. Disks 1 inch in diameter and 1/16 inch thick were pressed with the aid of paraffin-carbon tetrachloride binder. For each mixture two disks, one on top of the other, were placed on coarse zirconia sand sprinkled on a slab of silica brick. Firing was for 24 or 71 hours at 800° or 900° C, respectively. It was hoped that the bottom disk would act as a buffer for the upper test disk. In the specimens containing over 60%  $\text{B}_2\text{O}_3$ , however, the entire disk-pair flowed into and penetrated the zirconia placing sand, and rendered the specimens useless. There was also evidence of considerable loss of  $\text{B}_2\text{O}_3$  from volatilization.

The results of these experiments are presented in Table 2. No evidence for any intermediate compound was obtained. The firing temperatures of 800° and 900° C were apparently too low to reveal liquid immiscibility, if such does indeed exist. No reliable information on the location of the liquidus curve was obtained, because of the uselessness of the  $\text{B}_2\text{O}_3$  - rich specimens for this purpose. Anatase was converted to rutile at both 800° and 900° C.

Tentatively, it appears that the anatase - rutile transition lies below 800° C. Whether or not  $\text{B}_2\text{O}_3$  enters into the rutile thus formed is open to question. If it does, it would lower the transition temperature characteristic of pure  $\text{TiO}_2$ .

Samples containing 80, 85, 90, and 95%  $\text{B}_2\text{O}_3$  were next fired for 1 hour in a platinum crucible, a container having been found necessary in the preliminary runs.

TABLE 2

PRELIMINARY FIRINGS IN THE SYSTEM  $\text{TiO}_2\text{-B}_2\text{O}_3$ 

Composition (wt %)		Time (hrs)	Temp. (° C)	Phases Present
$\text{TiO}_2$	$\text{B}_2\text{O}_3$			
80	20	65½	900	Rutile + Glass
80	20	24	800	Rutile + Glass
60	40	65½	900	Rutile + Glass
60	40	24	800	Rutile + Glass
40	60	21½	900	Rutile + Glass
40	60	24	800	Rutile + Glass
20	80	1	1400	Rutile + 2 Glasses (?)
20	80	71	900	Rutile + Glass
20	80	24	800	Rutile + Glass
15	85	1	1400	Rutile + 2 Glasses (?)
15	85	71	900	Rutile + Glass
15	85	24	800	Rutile + Glass
	90	1	1400	Rutile + 2 Glasses (?)
10	90	71	900	Rutile + Glass
10	90	24	800	Rutile + Glass
5	95	1	1400	Rutile + 2 Glasses (?)
5	95	71	900	Rutile + Glass
5	95	24	800	Rutile + Glass

All four samples showed crystals and glass, suggesting that the liquidus curve crosses the 1400° C isotherm between 95% and 100% B<sub>2</sub>O<sub>3</sub>. This tentative conclusion is in need of further confirmation because 1 hour runs, although minimizing B<sub>2</sub>O<sub>3</sub> - volatilization, may not be sufficient to establish maximum solubility. There was some suggestion of liquid immiscibility in the 1400° runs. The glasses from these runs were brown in color and presented a finely-speckled appearance suggesting blebs of different refractive index than the matrix. In contrast, the glasses from the 900° and 800° runs were clear and colorless.

### III. THE SYSTEM ZrO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub>

No full-scale investigation of the system zirconia-boric oxide appears ever to have been carried out. Venable and Clarke<sup>14</sup> stated that zirconia is not attacked by molten boric oxide. Guertler<sup>2</sup> reported that ZrO<sub>2</sub> is not dissolved by B<sub>2</sub>O<sub>3</sub>. However, Foex<sup>3</sup> established the solubility of ZrO<sub>2</sub> at 1200° C as 0.90 moles in 100 moles of B<sub>2</sub>O<sub>3</sub>, equivalent to a weight percent solubility of 1.57. The liquidus curve in the ZrO<sub>2</sub>-B<sub>2</sub>O<sub>3</sub> system must therefore descend almost parallel to the B<sub>2</sub>O<sub>3</sub> composition vertical. Dietzel and Tober<sup>4</sup> left open the question of compound formation in the system, although the difference in field strength of B<sub>2</sub>O<sub>3</sub> (1.45) and ZrO<sub>2</sub> (0.78) lies well beyond the 0.30 limit regarded as the minimum required for compound formation. Baskin, Harada and Handwerk<sup>15</sup> encountered no new phase when several ZrO<sub>2</sub> : B<sub>2</sub>O<sub>3</sub> compositions were fired in air at 1200° C for 1 hour. The marked difference in ionic radius and in coordination number between zirconium and boron ions would suggest that molten mixtures of the two oxides might separate into two immiscible liquids<sup>6</sup>.

There is no unanimous agreement as to the polymorphic relations of zirconium dioxide. A useful review has recently been presented by Weber and Schwartz<sup>16</sup>. Most workers agree on the existence of at least two polymorphs, a low temperature

monoclinic form corresponding to the mineral baddeleyite, and a higher temperature higher density tetragonal form. Considerable variation exists in the temperatures assigned by different authors to this transition, although most values lie between 950 and 1250° C, the observed differences are apparently due to differences in technique employed to locate the transition, with a lesser effect produced by impurities (notably hafnia) in the  $ZrO_2$ . Recent work by Mumpton and Roy<sup>17</sup> on especially pure zirconia places the inversion at 1170° C. Lynch, Vahldiek and Robinson<sup>18</sup>, also working with pure  $ZrO_2$ , place it between 1182° and 1193° C, in essential agreement with Mumpton and Roy. Although a few workers<sup>19</sup> have maintained that tetragonal zirconia can be quenched through the inversion temperature to room temperature, most investigators agree that the inversion to the monoclinic form proceeds spontaneously, on cooling, causing cracking and destruction of the test specimen. There can be little doubt that tetragonal zirconia has been observed at low temperatures, as noted by Clark and Reynolds<sup>20</sup> and by Weber and Schwartz<sup>16</sup>. But in such instances it has formed metastably at low temperatures by thermal dissociation of zirconium salts, and changes monotropically to the stable monoclinic form upon heating to 500° or 600° C.

Several other forms of zirconia have also been reported. There is wide belief, although little or no direct evidence for it, that tetragonal zirconia inverts at 1700° to 1900° C to a cubic form, stable to the melting point of 2680° C. Cubic solid solutions of zirconia with  $MgO$ ,  $CaO$ , etc., are known, and these are believed to represent the stabilized cubic form. Wittels and Sherrill<sup>21</sup> have recently reported conversion of monoclinic  $ZrO_2$  into a cubic form at low temperatures by fast neutron bombardment. This they regard as equivalent to the alleged high temperature cubic form, and as existing metastably at low temperatures, changing to monoclinic zirconia when annealed at 800° C. Cohn<sup>22</sup> early suggested a hexagonal (trigonal) form produced by prolonged heating above 1900° C, which inverted to a pseudohexagonal

orthorhombic form at 625° C. This view has enjoyed little support, but recent work by Evans and Wildsmith<sup>23</sup> has revived the belief in a possible hexagonal form. Sense<sup>24</sup> has suggested the possibility that monoclinic zirconia reappears as a high-temperature phase above 2250° C. Much of the uncertainty existing in binary phase diagrams involving  $\text{ZrO}_2$  as one of the components can be traced to the uncertainties still remaining in the polymorphic relations of zirconia.

Some preliminary studies have been made in the system  $\text{ZrO}_2\text{-B}_2\text{O}_3$ . These had the same fourfold purpose as similar studies in the  $\text{TiO}_2\text{-B}_2\text{O}_3$  system, reported earlier. The experimental approach, too, was similar. Fine-grained  $\text{ZrO}_2$  was obtained by thermal decomposition of zirconium adipate at 300° to 400° C, followed by ignition over a blast-burner to burn off carbonaceous material. X-ray diffraction revealed the product to consist of a mixture of monoclinic and tetragonal (presumably metastable) zirconia. The compositions investigated, and the results obtained, are given in Table 3. Compositions high in  $\text{B}_2\text{O}_3$  were found to flow readily, and to run off the setting disks (three parts  $\text{ZrO}_2$  and 1 part kaolin). This was attributed to the partial hydration of the fused  $\text{B}_2\text{O}_3$  raw material on standing, to  $\text{H}_3\text{BO}_3$ , with resulting fluidity on firing. This behaviour led to the substitution of  $\text{H}_3\text{BO}_3$  for the partially hydrated  $\text{B}_2\text{O}_3$ , and to the use of a platinum crucible as container.

X-ray patterns of all test specimens revealed monoclinic  $\text{ZrO}_2$  as the only identifiable crystalline phase. No evidence for compound formation was obtained. No all-glass products were obtained, suggesting that the zirconia liquidus lies on the  $\text{B}_2\text{O}_3$  - rich side of the 5 zirconia: 95 boric oxide composition. Optical examination of the glass phase (marked with an asterisk in Table 3) of some of the runs suggested a two-liquid condition.

In a further attempt to test the possible existence of an intermediate compound, zirconyl nitrate was heated in a large excess (20:1) of  $\text{H}_3\text{BO}_3$  in a platinum crucible

TABLE 3

PRELIMINARY FIRINGS IN THE SYSTEM  $\text{ZrO}_2\text{-B}_2\text{O}_3$ 

Composition (wt %)		Time (hrs)	Temp. (° C)	Phases Present
$\text{ZrO}_2$	$\text{B}_2\text{O}_3$			
80	20	16½	900	Glass, $\text{ZrO}_2$ (Mono)
60	40	16½	900	Glass, $\text{ZrO}_2$ (Mono)
40	60	16½	900	(Sample Contaminated)
20	80	16½	900	(Sample Contaminated)
20	80	1½	1020	Glass,* $\text{ZrO}_2$ (Mono)
20	80	1	1183	Glass,* $\text{ZrO}_2$ (Mono)
20	80	1	1291	Glass,* $\text{ZrO}_2$ (Mono)
15	85	16½	900	(Sample Contaminated)
15	85	2	1010	Glass,* $\text{ZrO}_2$ (Mono)
15	85	1	1181	Glass,* $\text{ZrO}_2$ (Mono)
15	85	1	1291	Glass,* $\text{ZrO}_2$ (Mono)
10	90	16½	900	(Sample Contaminated)
10	90	1	1020	Glass,* $\text{ZrO}_2$ (Mono)
10	90	1	1175	Glass,* $\text{ZrO}_2$ (Mono)
5	95	16½	900	(Sample Contaminated)
5	95	1	1015	Glass,* $\text{ZrO}_2$ (Mono)
5	95	1	1175	Glass,* $\text{ZrO}_2$ (Mono)
5	95	1	1385	Glass,* $\text{ZrO}_2$ (Mono)

at 800° - 900° C for two weeks. Fused  $B_2O_3$  was added during the test to insure a large excess. During cooling of the crucible on removal from the furnace, crystals could be observed to develop. This observation suggests the necessity for quenching samples used to delineate the liquidus curve. The sample was leached with boiling water, and left a residue of monoclinic zirconia crystals 1 to 3 millimeters long.

#### IV. THE SYSTEM $HfO_2 - B_2O_3$

Very little phase equilibrium work has been published for systems in which  $HfO_2$  is one of the components. In general, hafnia shows close similarity to zirconia in physical and chemical properties. Like zirconia, it exhibits two polymorphic forms, a low temperature monoclinic form and a high temperature tetragonal form. According to Curtis, Doney and Johnson<sup>25</sup> the transition temperature is about 1700° C and involves a 3.4% density increase. This compares with a transition temperature of about 1180° C and a 7.5% density increase, for the corresponding zirconia inversion. These authors give  $2900^\circ \pm 25^\circ$  C as the melting point of  $HfO_2$ . A cubic form has also been reported<sup>26</sup>. Richardson, Scott and Shea<sup>27</sup> have synthesized  $HfSiO_4$ , isostructural with zircon ( $ZrSiO_4$ ). Indeed, natural zircon always contains some  $HfSiO_4$  in solid solution, amounting to about 2 percent (calculated as  $HfO_2$  in the  $ZrO_2$  extracted from the zircon). Durif<sup>28</sup> reports that both hafnia and zirconia form 1 : 1 compounds with  $GeO_2$ , and both  $HfGeO_4$  and  $ZrGeO_4$  possess the scheelite structure. As far as is known, no previous work has been reported on the  $HfO_2-B_2O_3$  system. In view of such similarities in behavior between  $HfO_2$  and  $ZrO_2$  as noted above, the  $HfO_2-B_2O_3$  might be expected to show great similarity to the system  $ZrO_2-B_2O_3$ . Thus, the discussion of the possibility of compound formation and liquid immiscibility in the system  $ZrO_2-B_2O_3$  applies equally well to the system  $HfO_2-B_2O_3$ .

A preliminary study of relations in the  $HfO_2-B_2O_3$  system has been undertaken. As in the  $TiO_2-B_2O_3$  and  $ZrO_2-B_2O_3$  studies, samples were fired in a platinum crucible



TABLE 4

PRELIMINARY FIRINGS IN THE SYSTEM  $\text{HfO}_2\text{-B}_2\text{O}_3$ 

Composition (wt. %)		Time (hrs)	Temp. (° C)	Phases Present
$\text{HfO}_2$	$\text{B}_2\text{O}_3$			
75	25	2	1400	Glass, $\text{HfO}_2$ (Mono)
20	80	2	1400	2 Glasses (?), $\text{HfO}_2$ (Mono)
15	85	2	1400	2 Glasses (?), $\text{HfO}_2$ (Mono)
15	85	5	1400	2 Glasses (?), $\text{HfO}_2$ (Mono)
10	90	2	1400	2 Glasses (?), $\text{HfO}_2$ (Mono)
5	95	2	1400	2 Glasses (?), $\text{HfO}_2$ (Mono)

because of the fluidity of the  $B_2O_3$  - rich compositions. The results of the few reconnaissance runs are given in Table 4. The only crystalline phase encountered was the monoclinic polymorph of hafnia. No evidence for an intermediate compound was found. The data from these  $1400^\circ$  runs suggests a liquidus curve close to the  $B_2O_3$  end of the system. There is strong evidence for liquid immiscibility in the system. The 2 hour run on the 15  $HfO_2$  : 85  $B_2O_3$  sample was particularly revealing in this connection. Small spherical pellets of high refractive index, and approximating 2 microns in size, were clearly visible in a low-index glassy matrix. These pellets were slightly anisotropic, showing a "uniaxial cross" effect characteristic of strained isotropic material. An acetic acid solution completely leached the low index matrix and freed the pellets. It was tentatively concluded from their shape and optical characteristics that these pellets represent a hafnia-rich glass. Other runs showed similar pellets, although these were so much smaller in size that they could not be clearly resolved under the microscope. A distinctly "dingy" appearance characteristic of micro-heterogeneous materials was shown in these runs. Results to date suggest that the syntectic horizontal (the lower limit of the two liquid area) must lie below  $1400^\circ$  C, and that the two liquid area extends from less than 5 percent hafnia to at least 20 percent hafnia.

#### V. THE SYSTEM $ThO_2$ - $B_2O_3$ - $Na_2O$

Our interest in this system arises from the possibility that  $B_2O_3$  or the various sodium borates might constitute practical fluxes for recrystallization of  $ThO_2$ . Two of the three limiting binary diagrams have been studied and phase diagrams have been published. Cole and Taylor<sup>29</sup> studied the  $Na_2O$ - $B_2O_3$  system in the temperature range  $1150^\circ$  -  $1400^\circ$  C. Morey and Merwin<sup>30</sup> published a phase diagram for the  $B_2O_3$  - rich portion of the system, and Morey<sup>31</sup> later presented a complete diagram. The system  $ThO_2$ - $B_2O_3$  has been the subject of several recent investigations. Rase<sup>32</sup>

recently published a tentative phase diagram, and Baskin, Harada and Handwerk<sup>33</sup> reported additional information on the compound  $\text{ThB}_2\text{O}_5$ . No diagram has been presented for the system  $\text{Na}_2\text{O}-\text{ThO}_2$ .

Because of the intermediate compound  $\text{ThB}_2\text{O}_5$ , boric oxide is not a practical solvent or flux for the low temperature growth of thorium crystals. It was decided to investigate the possibility of borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) as a low temperature flux for thorium. Accordingly, some preliminary runs were made in the  $\text{ThO}_2-\text{B}_2\text{O}_3-\text{Na}_2\text{O}$  system to determine if the compatibility triangle configuration is favorable. The samples studied, and the results obtained, are presented in Table 5.

Samples 2 and 3 were prepared from pure  $\text{ThO}_2$  and reagent grade sodium carbonate monohydrate; samples 1 and 4 from thorium and borax; samples 5, 6 and 8 from thorium, borax and boric oxide; samples 7 from thorium and sodium sulfate; and sample 9 from thorium and boric oxide.

It was first necessary to find out whether compounds exist along the  $\text{Na}_2\text{O}-\text{ThO}_2$  binary system, as this would affect the Alkemade line arrangement within the ternary diagram. The purpose of samples 2, 3, and 7 was to find out whether such a compound or compounds could be synthesized. Samples 2 and 3 gave no evidence of a compound. The X-ray pattern of sample 7 shows several small peaks which could not be matched with any compound listed in the A. S. T. M. card file. Optical examination of the same sample failed to disclose anything other than thorium and glass. Further attempts will be made to synthesize a compound in this binary system, but, except for the anomalous X-ray pattern of sample 7, the evidence thus far is against the existence of a compound.

Assuming there is no compound along the  $\text{Na}_2\text{O}-\text{ThO}_2$  side of the diagram, all the possible joins within the  $\text{ThO}_2-\text{B}_2\text{O}_3-\text{Na}_2\text{O}$  ternary diagram have been added to the sketch (Fig. 1).

TABLE 5

PRELIMINARY FIRINGS IN THE SYSTEM  $\text{ThO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$ 

Sample No	Composition (wt. %)			Time (hrs)	Temp. ( $^{\circ}\text{C}$ )	Phases Present
	$\text{Na}_2\text{O}$	$\text{ThO}_2$	$\text{B}_2\text{O}_3$			
1.	9.0	70.0	21.0	$\frac{1}{2}$	900	$\text{ThO}_2$ , Glass
2.	21.0	79.0	----	$\frac{1}{2}$	900	$\text{ThO}_2$ , $\text{Na}_2\text{CO}_3$
3.	(ThO <sub>2</sub> in excess $\text{Na}_2\text{CO}_3$ )			$2\frac{1}{2}$	1000-1100	$\text{ThO}_2$ , $\text{Na}_2\text{CO}_3$
4.	28.5	7.0	64.5	5	750-800	$\text{ThO}_2$ , Glass, $\text{Na}_2\text{B}_4\text{O}_7$
5.	11.5	48.5	40.0	5	750-800	$\text{ThO}_2$ , Glass, $\text{Na}_2\text{B}_6\text{O}_{10}$ (?)
6.	11.5	37.0	51.5	5	750-800	$\text{ThO}_2$ , Glass, $\text{Na}_2\text{B}_8\text{O}_{13}$ (?)
7.	21.0	79.0	----	2	1400	$\text{ThO}_2$ , Glass, Unident. Phase
8.	15.0	13.0	72.0	2	1400	$\text{ThB}_2\text{O}_5$ , $\text{ThO}_2$ , Two Glasses (?)
9.	(ThO <sub>2</sub> in excess $\text{B}_2\text{O}_3$ )			5	1400	$\text{ThB}_2\text{O}_5$ , Two Glasses (?)

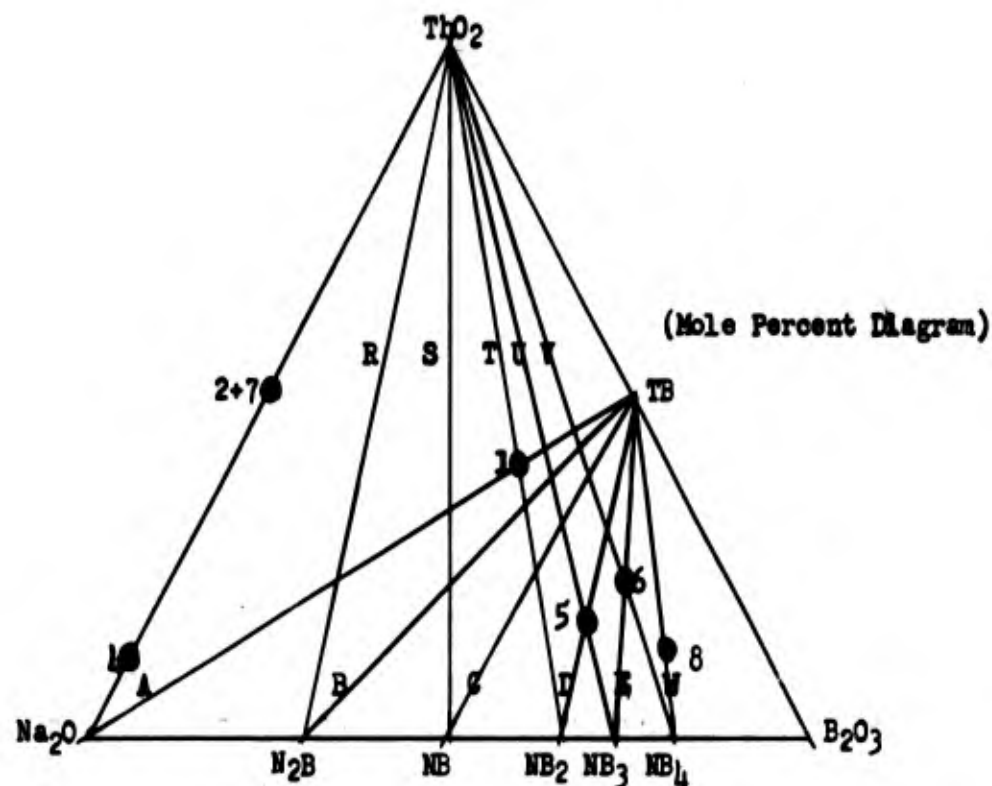


FIGURE 1

Diagram Showing all of the Theoretically Possible Compatibility Joins in the System  $\text{ThO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$ .

Tentatively, the results tabulated in Table 5 may be interpreted thus: Sample 1 eliminates joins A, B, and C; sample 5 eliminates join D; sample 6 eliminates join E; sample 8 confirms join W.

It is not certain that samples 5 and 6 were fired long enough for  $\text{ThB}_2\text{O}_5$  to form from the particular compositions used; however, Base's success in synthesizing  $\text{ThB}_2\text{O}_5$  at  $325^\circ\text{C}$  in two hours is reassuring. Thus, it appears that the actual arrangement of joins within the  $\text{ThO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$  system is as shown below in Figure 2.

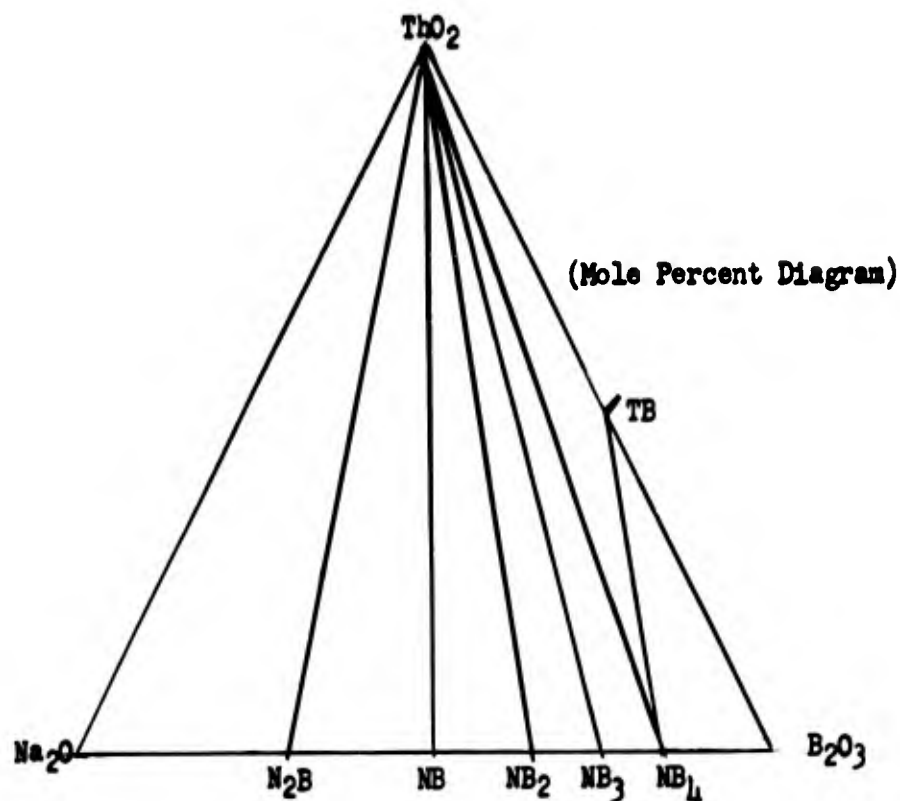


FIGURE 2

Tentative Compatibility Joins in the System  $\text{ThO}_2\text{-B}_2\text{O}_3\text{-Na}_2\text{O}$ .

Since the  $\text{N}_2\text{B}$  to  $\text{ThO}_2$  join is valid, any compound, which, in the future, may be found in the  $\text{Na}_2\text{O-ThO}_2$  binary system can be joined only with  $\text{N}_2\text{B}$ .

The liquid immiscibility evident in sample 8 will bear further investigation. If the  $\text{ThB}_2\text{O}_5$  crystals represent quench growth, then the eutectic between  $\text{NB}_4$  (m.p.  $816^\circ\text{C}$ ) and TB (m.p.  $1483^\circ\text{C}$ ) lies, in the ternary diagram, between sample 8 and  $\text{NB}_4$ , and sample 8 lies in a two-liquid area. Liquid immiscibility was also observed in sample 9.

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